Disorder and chain superconductivity in $YBa_2Cu_3O_{7-\delta}$

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The effects of chain disorder on superconductivity in $YBa_2Cu_3O_{7-\delta}$ are discussed within the context of a proximity model. Chain disorder causes both pair breaking and localization. The hybridization of chain and plane wave functions reduces the importance of localization, so that the transport anisotropy remains large in the presence of a finite fraction δ of oxygen vacancies. Penetration depth and specific heat measurements probe the pair breaking effects of chain disorder, and are discussed in detail at the level of the self-consistent *T*-matrix approximation. Quantitative agreement with these experiments is found when chain disorder is present. [S0163-1829(99)10105-X]

Current understanding of the low-energy electronic excitation spectrum of $YBa_2Cu_3O_{7-\delta}$ (YBCO) is incomplete. As with other high-T_c superconductors, YBCO is a layered compound in which the CuO_2 layers are conducting, strongly correlated quasi-two-dimensional electron gasses. The CuO_2 layers have been extensively studied[1] in $Bi_2Sr_2CaCu_2O_8$ using angle-resolved photoemission. While in-plane conductivity measurements[2] suggest strong similarities between the CuO_2 planes in $Bi_2Sr_2CaCu_2O_8$ and YBCO, a complete description of YBCO is complicated by the presence of conducting one-dimensional CuO chain layers, about which relatively little is known.

Since the CuO chains are unique to the YBaCuO family of superconductor, one expects to find their signature in a variety of experiments. Tunneling experiments,[3] for example, reveal a finite density of states (DOS) at the Fermi energy in the superconducting state, in contrast to $Bi_2Sr_2CaCu_2O_8$ where a clear *d*-wave-like gap is observed.[4] Measurements of the penetration depth λ_c along the *c* axis (perpendicular to the layers) find a power-law dependence on temperature which is material dependent.[5–7] More dramatically, a well developed pseudogap[8] is found in the *c*-axis optical conductivity of $YBa_2Cu_3O_{7-\delta}$ (Ref. 9) and $YBa_2Cu_4O_8$,[8] but not in $La_{2-x}Sr_xCuO_4$.[8,10] In some cases, such as in-plane anisotropic conductivity measurements,[2] it is straightforward to distinguish the contributions of the chains from those of the planes. In general, however, the influence of the chains is not trivial to understand. Calculations based on multiband models suggest, for example, that interband transitions between the plane and chain bands dominate the *c*-axis conductivity,[11] and that the pseudogap seen in optical conductivity experiments reflects a shift in interband transition energies due to the opening of a gap[12] in the CuO_2-layer Fermi surface. These predictions are quite different from those of one-band models,[13–15] in which disorder and inelastic scattering are assumed to play a key role in *c*-axis transport. For this reason, it is essential to develop a model which correctly describes the low-energy physics of the chain-plane system.

Evidence concerning the chain electronic structure is indirect. In $YBa_2Cu_3O_{7-\delta}$, the chains are not continuous, but are broken into segments of finite length by the fraction δ of vacant chain oxygen sites. In spite of this, there is a large anisotropy in the in-plane conductivity,[2] indicating that the chains are metallic. The absence of localization suggests that electronic states associated with the chains, while highly anisotropic, are not one-dimensional. In the superconducting state, the in-plane anisotropy[16] in the penetration depth λ is nearly identical in magnitude to the conductivity anisotropy, suggesting a significant superfluid density on the chain layer for temperatures $T \ll T_c$. What is truly remarkable, however, is that the temperature dependence of the chain superfluid density—as measured in penetration depth experiments[17]—is almost the same as that of the planes. The apparent similarity of the excitation spectra in the chain and plane layers is surprising given that the underlying bands have completely different structures.

Several different models have been proposed to describe chain superconductivity. The simplest model consistent with *d*-wave chain superconductivity is the proximity model, in which the pairing interaction resides in the CuO_2 planes and chain superconductivity occurs through the hybridization of plane and chain wave functions. The failure of this model (discussed below) to describe penetration depth experiments,[18] has led several authors[19–21,11] to abandon the premise of a pairing interaction contained exclusively within the CuO_2 planes.

In this work, we show that a small amount of chain disorder is sufficient to reconcile the proximity model with experiments. We model a CuO_2-CuO-CuO_2 trilayer with a three-band tight-binding Hamiltonian in which the isolated chain and plane layers have one- and two-dimensional dispersions, respectively, coupled through single electron hopping. The resultant bands are three-dimensional hybrids of chain and plane states. Because the hybridization is weak for some values of the in-plane momentum **k**, localization effects are present, but are not sufficient to eliminate quasiparticle transport in the chains. We discuss disorder effects in chain superconductivity in the context of two different experimental probes of the low-energy DOS: specific-heat measurements,[22] and penetration depth anisotropy measurements.[17]

We consider a single trilayer with periodic boundary conditions along the *c* axis. The annihilation operator for an electron in layer *i* with two-dimensional wave-vector **k** and

spin σ is $c_{i\mathbf{k}\sigma}$. The mean-field Hamiltonian for such a model is (using the Nambu spinor notation) $\mathcal{H}=\Sigma_{\mathbf{k}} C_{\mathbf{k}}^{\dagger}\mathbf{H}_{\mathbf{k}}C_{\mathbf{k}}$ with

$$\mathbf{H}_{\mathbf{k}}=\begin{bmatrix} \xi_{1\mathbf{k}} & t_{\perp 1} & t_{\perp 2} & \Delta_{\mathbf{k}} & 0 & 0 \\ t_{\perp 1} & \xi_{1\mathbf{k}} & t_{\perp 2} & 0 & \Delta_{\mathbf{k}} & 0 \\ t_{\perp 2} & t_{\perp 2} & \xi_{2\mathbf{k}} & 0 & 0 & 0 \\ \Delta_{\mathbf{k}} & 0 & 0 & -\xi_{1-\mathbf{k}} & -t_{\perp 1} & -t_{\perp 2} \\ 0 & \Delta_{\mathbf{k}} & 0 & -t_{\perp 1} & -\xi_{1-\mathbf{k}} & -t_{\perp 2} \\ 0 & 0 & 0 & -t_{\perp 2} & -t_{\perp 2} & -\xi_{2-\mathbf{k}} \end{bmatrix} \tag{1}$$

and $C_{\mathbf{k}}^{\dagger}=[c_{1\mathbf{k}\uparrow}^{\dagger}c_{2\mathbf{k}\uparrow}^{\dagger}c_{3\mathbf{k}\uparrow}^{\dagger}c_{1-\mathbf{k}\downarrow}c_{2-\mathbf{k}\downarrow}c_{3-\mathbf{k}\downarrow}]$. The hopping amplitude $t_{\perp 1}$ describes hopping between adjacent CuO_2 planes and $t_{\perp 2}$ describes hopping between plane and chain layers. The dispersions $\xi_{1\mathbf{k}}$ and $\xi_{2\mathbf{k}}$ describe the isolated plane and chain layers, respectively, while $\Delta_{\mathbf{k}}$ is the superconducting order parameter for the plane layer, which is taken to have *d*-wave symmetry. It has been suggested[23] that a suitable tight-binding model for the plane band is

$$\xi_{1\mathbf{k}}=-2t_1[\cos k_x a+\cos k_y a+2t'\cos k_x a\cos k_y a + t''(\cos 2k_x a+\cos 2k_y a)]-\mu_1 \tag{2}$$

with $t'=-0.2$ and $t''=0.25$, and $a\approx 3$ Å the lattice constant. The chain layer is modeled by

$$\xi_{2\mathbf{k}}=-2t_2\cos k_y a-\mu_2. \tag{3}$$

The parameters t_1 and t_2 can be determined with some certainty from the magnitudes of the *a* (in-plane, perpendicular to chains) and *b* axis (parallel to chains) penetration depths.[16] The other parameters are not as easily determined, but are constrained by requiring that the Fermi surfaces be consistent with those of band-structure calculations.[23] Ultimately, our conclusions are not sensitive to the choice of parameters provided the above constraints are met. We take, as plausible: $\{t_1,t_2,\mu_1,\mu_2,t_{\perp 1},t_{\perp 2}\}=\{60,400,-20,-600,40,60\}$ meV. It should be emphasized here that the chain bandwidth, $4t_2$, determined from $\lambda_b(T=0)$ is very near to that predicted by band-structure calculations,[23] consistent with the findings of positron annihilation studies.[24]

The order parameter is phenomenological, with

$$\Delta_{\mathbf{k}}=\Delta_0(T)[g(k_x)-g(k_y)], \tag{4}$$

where the temperature dependence is given by[25] $\Delta_0(T)/\Delta_0(0)=\tanh[T_c\Delta_0(T)/T\Delta_0(0)]$. Based on the location of the van Hove singularities in the tunneling DOS,[3] we estimate $\Delta_0=11$ meV. Furthermore, we find that taking $g(k)=\cos(ka)-0.3\cos(3ka)$ gives approximately the correct slope[17] for $\lambda_a(T)$ at low *T*.

As we shall see, band structure plays a central role in determining the effects of chain disorder. The bands (labeled **a**, **b**, and **c**) have dispersions given by the positive eigenvalues of $\mathbf{H}_{\mathbf{k}}$. In the normal state, $\epsilon_{\mathbf{k}}^{a}=\xi_{\mathbf{k}}^{-}$, $\epsilon_{\mathbf{k}}^{b}=\epsilon_{\mathbf{k}}^{-}$, and $\epsilon_{\mathbf{k}}^{c}=\epsilon_{\mathbf{k}}^{+}$ where

$$\epsilon_{\mathbf{k}}^{\pm}=\frac{\xi^{+}+\xi_2}{2}\pm\sqrt{\left[\frac{\xi^{+}-\xi_2}{2}\right]^2+2t_{\perp 2}^2}, \tag{5}$$

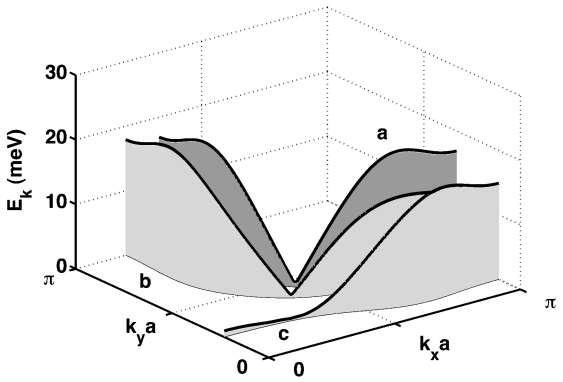

FIG. 1. Superconducting quasiparticle excitation energy $E_{\mathbf{k}}$ along the normal-state Fermi surfaces. The spectrum reflects both the *d*-wave structure of the order parameter, and the structure of the underlying band.

and where $\xi_{\mathbf{k}}^{\pm}=\xi_{1\mathbf{k}}\pm t_{\perp 1}$ are the energies of bonding and antibonding combinations of the two planes. From Eq. (5), it is clear that only the antibonding band mixes with the chain band, and that the bonding band (band **a**) is completely planelike. In Fig. 1, we show the **k**-dependent gap in the superconducting excitation spectrum, plotted along the Fermi surfaces of the normal-state bands. Band **a** has the gap structure expected for a *d*-wave superconductor in a tetragonal system. Bands **b** and **c** have a more complicated spectrum, reflecting the structure of the underlying bands.

It is simplest to start with a discussion of impurity effects in the normal state. Band **a** is unaffected by chain disorder, and we focus our attention on bands **b** and **c**. First, we emphasize that the behavior of the two bands, given by Eq. (5), depends on the degree of chain-plane hybridization, as characterized by

$$\alpha_{\mathbf{k}}=\frac{\sqrt{2}t_{\perp 2}}{|\xi_{2\mathbf{k}}-\xi_{\mathbf{k}}^{+}|}. \tag{6}$$

In the limit $\alpha_{\mathbf{k}}\gg 1$, the bands are degenerate relative to the coupling parameter $t_{\perp 2}$ and $\epsilon_{\pm}\approx(\xi_{2\mathbf{k}}+\xi_{\mathbf{k}}^{+})/2\pm\sqrt{2}t_{\perp 2}$. This is the standard result for the level repulsion of a degenerate two-level system. The wave functions in this limit are even and odd combinations of the antibonding and chain wave functions, and the electron tunnels between the bands with a frequency

$$\hbar/\tau_{\mathbf{k}}=2\sqrt{2}t_{\perp 2}\quad(\alpha_{\mathbf{k}}\gg 1). \tag{7}$$

On time scales longer than $\tau_{\mathbf{k}}$, bands **b** and **c** are three-dimensional. In the limit $\alpha_{\mathbf{k}}\ll 1$, on the other hand, $\epsilon_{\mathbf{k}}^{b}\approx\min(\xi_{2\mathbf{k}},\xi_{\mathbf{k}}^{+})-\alpha_{\mathbf{k}}\sqrt{2}t_{\perp 2}$, $\epsilon_{\mathbf{k}}^{c}\approx\max(\xi_{2\mathbf{k}},\xi_{\mathbf{k}}^{+})+\alpha_{\mathbf{k}}\sqrt{2}t_{\perp 2}$, and the wave functions for bands **b** and **c** are predominantly planelike or chainlike. The tail of band **c** near $k_x=0$, for example, is described by this limit. This weak mixing of chain and antibonding bands leads to a tunneling rate

$$\hbar/\tau_{\mathbf{k}}\approx\sqrt{2}t_{\perp 2}\alpha_{\mathbf{k}},\quad(\alpha_{\mathbf{k}}\ll 1) \tag{8}$$

which is much smaller than that of the degenerate case. In our trilayer model, $\alpha_{\mathbf{k}}$ is strongly **k** dependent due to the different structures of the (one-dimensional) chain and (two-dimensional) plane dispersions.

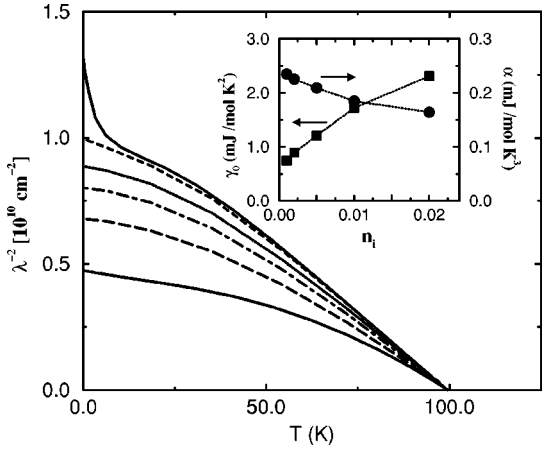

FIG. 2. Temperature dependence of the penetration depth. Solid curves are $\lambda_b^{-2}(T)$ (upper curve) and $\lambda_a^{-2}(T)$ (lower curve) for $n_i=0$. Other curves are for $\lambda_b^{-2}(T)$ for impurity concentrations $n_i=0.001$, $n_i=0.005$, $n_i=0.01$, and $n_i=0.02$ from top to bottom. $\lambda_a^{-2}(T)$ is almost unchanged by chain disorder. Inset: Dependence of the coefficients of the low-temperature specific heat on n_i.

Because of the large variation in the tunneling rate $\hbar/\tau_{\mathbf{k}}$, the effects of chain disorder are $\mathbf{k}$ dependent. If the average length of unbroken chain is l, then we can estimate the scattering rate to be $\tau_{tr}^{-1}=v_F/l$, where v_F is the Fermi velocity in the chain layer. States for which the tunneling rate $\tau_{\mathbf{k}}^{-1}$ between layers is much larger than the impurity scattering rate τ_{tr}^{-1} are considered three-dimensional, and are not susceptible to localization. On the other hand, chainlike states for which $\tau_{\mathbf{k}}^{-1}<\tau_{tr}^{-1}$ are susceptible to localization. In our trilayer model, only a small fraction of chain electrons are localized by chain disorder. This observation provides a natural explanation for the large conductivity anisotropy[2] seen in oxygen deficient YBCO.

We now turn our attention to the superconducting state. In Fig. 1 we show the $\mathbf{k}$-dependent superconducting gap (defined as the energy required to excite a quasiparticle at the Fermi surface with wave vector $\mathbf{k}$) produced by the pairing interaction in the CuO_2 plane layers. The low-energy tail in band $\mathbf{c}$ near $k_x=0$ is of particular importance for the current discussion. States in this part of the band are predominantly chainlike, and the gap is

$$E_{\mathbf{k}}^c \approx |\Delta_{\mathbf{k}}|\alpha_{\mathbf{k}}^2 \quad (\alpha_{\mathbf{k}} \ll 1). \tag{9}$$

These low-lying states have a significant influence on the low-T properties of the system. In Fig. 2 the clean-limit temperature-dependent penetration depth has a pronounced upturn in $\lambda_b^{-2}(T)$ at low temperatures. This reflects a sudden increase in the chain-layer superfluid density as T is lowered through $E_{\mathbf{k}}^c$.

The low-temperature upturn in λ_b^{-2} is a generic feature[18,19] of proximity models of $YBa_2Cu_3O_{7-\delta}$, although the onset temperature for the upturn depends on the details of the model. In this work, we show that small amounts of chain disorder eliminate the upturn. This is easily anticipated, since it is apparent that the states which have a small superconducting gap are chainlike, and are therefore strongly affected by chain disorder. The effects of disorder are twofold: localization (discussed above) and pair breaking. Pair breaking occurs for chainlike states whose binding energy $E_{\mathbf{k}}^c$ is less than the scattering rate $\hbar/\tau_{tr}$. Chainlike states are characterized by $\alpha_{\mathbf{k}} \ll 1$, and in this limit $E_{\mathbf{k}}^c$ is always smaller than the tunneling rate $\hbar/\tau_{\mathbf{k}}$ (assuming that $\Delta_{\mathbf{k}}<\sqrt{2}t_{\perp 2}$). This means that any Cooper pair which satisfies the criterion $\tau_{tr}^{-1}>\tau_{\mathbf{k}}^{-1}$ for localization is also broken by disorder.

Localization effects will therefore be important in probes of quasiparticle transport. However, since the penetration depth is a measure of dc superfluid transport, the important effect of chain disorder is pair breaking, which in this work is treated in the unitary limit of the self-consistent T-matrix approximation. The calculation is standard,[26] except for the fact that the impurities reside only in the chain layer. In the Nambu notation, the self-energy $\hat{\boldsymbol{\Sigma}}(\omega)$ is a sparse 6×6 matrix with nonzero elements connecting states in the chain layer only. The penetration depth then follows from

$$\lambda_\mu^{-2}(0)-\lambda_\mu^{-2}(T)=-\frac{4\pi e^2}{c^2}\frac{1}{\beta}\sum_n \frac{1}{\Omega}\sum_{\mathbf{k}} \mathrm{Tr}[\mathbf{G}(\mathbf{k},i\omega_n) \times \boldsymbol{\gamma}_\mu(\mathbf{k})\mathbf{G}(\mathbf{k},i\omega_n)\boldsymbol{\gamma}_\mu(\mathbf{k})], \tag{10}$$

where Tr is the trace over the 6×6 matrix contained in the square brackets, $\mathbf{G}(\mathbf{k},i\omega_n)=[i\omega_n-\mathbf{H}_{\mathbf{k}}-\hat{\boldsymbol{\Sigma}}(i\omega_n)]^{-1}$, and $\boldsymbol{\gamma}_\mu(\mathbf{k})=\hbar^{-1}\partial\mathbf{H}_{\mathbf{k}}/\partial k_\mu$. We emphasize that while this approach is reasonable for making predictions of superfluid and normal-fluid densities, it cannot describe the enhanced backscattering leading to localization of the normal fluid.[27]

In Fig. 2 we show the effect of disorder on $\lambda_b^{-2}(T)$ for different concentrations n_i of unitary scatterers. We see that even small amounts of disorder are sufficient to eliminate the upturn at low T. Chain disorder, on the other hand, has almost no effect on $\lambda_a^{-2}(T)$. In $YBa_2Cu_3O_{7-\delta}$, the scattering results from a fraction δ of chain oxygen sites which are vacant. Unfortunately, one cannot simply equate δ with the fractional impurity density n_i introduced below because of the tendency of oxygen vacancies to cluster. Instead, it is more useful to consider the average length of undamaged chain l (where $l=a/n_i$) as the fundamental measure of chain disorder.

A useful, and complementary, test of the model comes from examining the low-T specific heat C_v, which provides a direct measure of the quasiparticle density. For d-wave superconductors, the electronic contribution to C_v is well fitted by

$$C_v=\gamma_0 T+\alpha T^2, \tag{11}$$

where γ_0 is proportional to the normal-fluid density, and α depends on the $\mathbf{k}$ dependence of $\Delta_{\mathbf{k}}$ near the gap nodes. We evaluate γ_0 and α by fitting the DOS near the Fermi surface to $N(\omega)=N_0+N_1|\omega|$, and then evaluating $\gamma_0=N_0N_ak_B^2\pi^2/6$ mJ/mol/K^2, and $\alpha=9N_1N_ak_B^3\zeta(3)$ mJ/mol/K^3, where N_a is Avogadro's number, k_B is Boltzmann's constant, and $\zeta(n)$ is the Riemann ζ function. In the inset in Fig. 2 we show the effect of chain disorder on both γ_0 and α. We see that γ_0 increases rapidly with chain disorder, as a result of the increasing normal-fluid density. These results are in excellent quantitative agreement with experiments on high-quality single crystals,[22] where γ_0 was found to be 1–3 mJ/mol/K^2 for δ between 0.01 and 0.05.

Finally, we comment that we expect impurities to have little effect in *c*-axis transport, since the states which carry most of the current along the *c* axis are those which are most three-dimensional, and therefore are least affected by chain disorder. In a series of conductivity experiments on Zn-doped samples, Wang *et al.*[28] have found that while the *a*-*b* anisotropy is strongly affected by small amounts of Zn, the *c*-axis conductivity is almost unchanged.

In summary, we have shown that chain superconductivity in $YBa_2Cu_3O_{7-\delta}$ is well described by a proximity model, if one accounts for the presence of disorder in the chain layer. Within such a model, hybridization of the chain and plane layers is strongly dependent on the in-plane momentum **k**, so that while most electronic states are three-dimensional, a fraction of chainlike states are quasi-one-dimensional and susceptible to localization. We calculate the superfluid density in a self-consistent *T*-matrix approximation which captures the pair breaking effects of disorder, and find good agreement with both penetration depth[17] and specific heat[22] measurements.

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